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## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TOSHIBA BATTERY CO LTD

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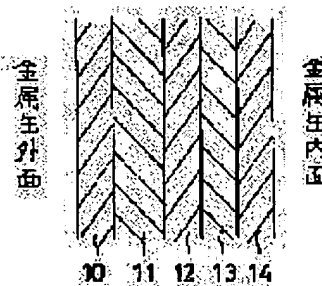
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## (54) ALKALINE BATTERY

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide an alkaline battery whose properties are not deteriorated during a long time storage by improving a container of the alkaline battery.

SOLUTION: In an alkaline battery produced by filling a bottomed cylindrical metal can, which works also as a cathode terminal, with an electricity generating element, a metal can manufactured by the following steps is used as the metal can: forming a nickel-iron diffused layer 12 and a nickel-tin alloy layer 13 successively in the side, which becomes the inner face of a can, of a cold rolled steel sheet base, forming a nickel-iron diffused layer 10 in the side, which becomes the outer face of the can, press-drawing the resultant steel sheet into a bottomed cylindrical can, and then forming a conductive layer 14 mainly consisting of graphite on the nickel-tin alloy layer 13 in the can inner face side. Consequently, a battery whose properties are not deteriorated can be manufactured and especially, the battery is more efficient in the case the graphite addition ratio to the cathode active mix is controlled to be 8% or less for high capacity.



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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to an alkaline cell.

[0002]

[Description of the Prior Art] After carrying out drawing processing of that by which the positive-electrode container performed nickel plating to both sides of a steel plate beforehand conventionally while the use of super-heavy loading, such as portable AV equipments, such as a notebook sized personal computer, a CD player, MD player, and a liquid crystal television, and a cellular phone, and heavy loading had been required of the latest alkaline cell or carrying out spinning only with a steel plate, the electric conduction film which performs nickel plating and makes a graphite a principal component at an inside, respectively is formed.

[0003] Since a crack will be produced on a nickel-plating front face and iron natural complexion will be exposed to it if drawing processing is carried out to a container when nickel plating is beforehand performed to a steel plate, contact resistance goes up compared with the conditions which the surface area of nickel plating decreases, therefore are altogether covered by nickel plating. Moreover, although nickel plating is performed to a superficies side when it extracts only with a steel plate and nickel plating is performed later, plating is attached to an inside side and the surroundings are bad. For example, if nickel plating is performed to a superficies side by the thickness of 3 micrometers, an inside side will become the thickness of about 0.5 micrometers. for this reason, a positive electrode -- contact to a mixture is bad, contact resistance becomes high, a short-circuit current falls, in long-term storage, degradation of a performance is caused and the yield of hydrogen gas also increases In order to solve these troubles, the electric conduction film which makes a graphite a principal component is formed in the positive-electrode container inside.

[0004]

[Problem(s) to be Solved by the Invention] However, these cures are insufficient and it is necessary to improve further for the use of super-heavy loading mentioned above. especially -- a high-capacity-izing sake -- a positive electrode -- a mixture -- the case where the inner rate of graphite addition is made into 8% or less -- a can inside and a positive electrode -- since contact resistance with a mixture becomes high, the need of improving further is high

[0005] this invention coped with the above-mentioned problem, was made, adds improvement about the container of an alkaline cell, and aims at offering the alkaline cell which does not produce performance degradation in long-term storage.

[0006]

[Means for Solving the Problem] In this invention, the following improvement was added to the container of an alkaline cell, and the above-mentioned purpose was attained. Namely, this invention is set to the alkaline cell which inner-\*(ed) the power generation element in the metal can of the closed-end cylindrical shape which serves as a positive-electrode terminal. As the above-mentioned metal can, a nickel-iron diffusion layer and a nickel-tin alloy layer are given to the side which becomes the can inside of a cold-rolled-steel-plate material base one by one. After giving a nickel-iron diffusion layer to the side which becomes can superficies and carrying out drawing processing of this at the shape of a closed-end cylindrical can, it is characterized by using the thing in which the electric conduction film which makes a graphite a principal component was formed on the nickel-tin alloy layer by the side of a can inside.

[0007] As described above, a stiff surface of metal is obtained very much by having given the nickel-tin alloy layer on it further with the nickel-iron diffusion layer on the steel plate base. a crack with a surface nickel-tin

alloy layer very fine to a stiff sake at the time of drawing processing -- generating -- a fine uneven side -- constituting -- a positive electrode -- it contributes to the improvement in contact with a mixture Moreover, since a nickel-iron diffusion layer is further under the nickel-tin alloy layer which the crack generated, the natural complexion of a steel plate is not exposed. Therefore, contact resistance is large, with a bird clapper, there is nothing and improvement in a short-circuit current can be aimed at.

[0008] Moreover, by this invention, although there are a fall of open circuit voltage and generating of hydrogen gas and it becomes a cell property top problem because the dissolution of the tin in an alloy layer takes place when the nickel-tin alloy layer is exposed, since the electric conduction film which makes a graphite a principal component is formed in the portion which the electrolytic solution of a positive-electrode container inside contacts, the dissolution of tin is prevented, the fall of open circuit voltage is prevented, and a short-circuit current improves further.

[0009] Moreover, since the superficies of the can which is a terminal-cum-the container which inner-\*\* a power generation element are being worn by the nickel-iron diffusion layer, compared with the usual nickel plating, contact resistance is low, and a nickel-iron diffusion layer also has the merit that a blemish cannot be attached very easily for a stiff reason.

[0010]

[Embodiments of the Invention] Hereafter, drawing explains the example in detail. Drawing 1 is the cross section of the JIS LR6 type (single 3 type) alkaline cell which is one example of this invention. Moreover, drawing 2 is drawing showing the cross-section structure of the metal can 1 of the alkaline cell of drawing 1.

[0011] the metal can of the closed-end cylindrical shape to which 1 serves as a positive-electrode terminal in drawing 1, and 2 -- a positive electrode -- a mixture and 3 -- for a negative-electrode current collection rod and 6, as for a ring-like metal plate and 8, an insulating gasket and 7 are [ separator and 4 / a gel negative electrode and 5 / a metal obturation board and 9 ] label jackets Moreover, in drawing 2, 10 is an electric conduction membrane layer to which in a steel plate and 12 a nickel-iron diffusion layer and 13 make a graphite as a nickel-tin alloy layer, and 14 makes [ a nickel-iron diffusion layer and 11 ] it a principal component.

[0012] The metal can 1 which is a terminal-cum-the container of the cell of drawing 1 is manufactured as follows, and serves as composition as shown in drawing 2. That is, the cold-rolled-steel-plate material 11 is processed with plating processing, heat treatment, etc., the nickel-iron diffusion layer 12 and the nickel-tin alloy layer 13 are formed in the direction which is on the inside side of a container, and the nickel-iron diffusion layer 10 is formed in a superficies side. Thus, drawing processing of what was formed is carried out at the cylindrical shape of an owner bottom, and the electric conduction film which makes a graphite a principal component is formed in the portion except the part which touches the gasket of opening at an inside after processing it in the shape of [ of a closed-end cylindrical shape ] a can. The method of application of an electric conduction film dilutes the conductive coating material which makes a graphite a principal component with low-boiling point organic solvents, such as a methyl ethyl ketone (MEK), and applies it to a metal-can inside in the shape of a fog from a spray gun. The portion which touches the gasket of metal-can opening is made not to be applied. After applying conductive coating material with a spray gun, a solvent is evaporated with a dryer. The thickness of the remaining electric conduction film has desirable about 1-10 micrometers.

[0013] the positive electrode which carried out pressing to the shape of a cylinder into this metal can 1 -- it fills up with the mixture 2 a positive electrode -- a mixture 2 mixes the manganese dioxide powder and a graphite powder, contains this in a metal can 1, and it carries out pressing to the shape of a hollow cylinder by the predetermined pressure a high-capacity-izing of service capacity sake -- a positive electrode -- the rate of graphite addition in a mixture 2 ([graphite-powder weight] / [a manganese dioxide weight + graphite-powder weight]) was made into 8% moreover, a positive electrode -- the centrum of a mixture 2 is filled up with the gel negative electrode 4 through the separator 3 of the shape of a closed-end cylinder which consists of a nonwoven fabric of an acetalization vinylon In the gel negative electrode 4, the negative-electrode current collection rod 5 made from brass is inserted so that the upper-limit section may be projected from the gel negative electrode 4. The insulating gasket 6 which becomes the lobe peripheral face of the negative-electrode current collection rod 5 and the up inner skin of a metal can 1 from double annular polyamide resin is arranged. Moreover, the ring-like metal plate 7 is arranged between the double annular sections of a gasket 6, and it is arranged by the metal plate 7 so that the metal obturation board 8 of a hat form which serves as a negative-electrode terminal may contact the head of the current collection rod 5. And the seal mouth of the inside of a metal can 1 is carried out with the gasket 6 and the metal obturation board 8 by making the opening edge of a metal can 1 crooked in the

inner direction.

[0014] (Example 1 of comparison) Except not forming the electric conduction film which considers as a terminal-cum-the container which inner-\*\* a power generation element, and makes a graphite a principal component at an inside, the same can as an example was used and the JIS LR6 type (single 3 type) alkaline cell was assembled like the example.

[0015] (Example 2 of comparison) Drawing processing of what considered as a terminal-cum-the container which inner-\*\* a power generation element, performed nickel plating to the inside side of cold-rolled-steel-plate material beforehand, and performed nickel plating also to the superficies side was carried out at the shape of a can of a closed-end cylindrical shape, and the can in which the electric conduction film which makes a graphite a principal component was formed was further used for the inside. The JIS LR6 type (single 3 type) alkaline cell was assembled like the example except it.

[0016] (Example 3 of comparison) After considering as a terminal-cum-the container which inner-\*\* a power generation element and carrying out drawing processing of the cold-rolled-steel-plate material at the shape of a can of a closed-end cylindrical shape, nickel plating was performed, and the can in which the electric conduction film which makes a graphite a principal component was formed was used for the inside. LIS specification LR6 type (single 3 type) alkaline cell was assembled like the example except it.

[0017] About each alkaline cell assembled as mentioned above, the open circuit voltage (n= 100 averages) ten days and after storing for 60 days, a short-circuit current (n= 100 averages), and amount [of hydrogen gas underwater decomposed at 60 degrees C, and uptake] (n= 100 averages) was investigated for the gas inside a cell. These results are shown in a table.

[0018]

[Table 1]

60℃貯蔵	開路電圧 (V)		短絡電流 (A)		水素ガス量 (CC)	
	10日後	60日後	10日後	60日後	10日後	60日後
実施例	1. 610	1. 594	14. 0	12. 5	0. 34	0. 56
比較例 1	1. 610	1. 583	9. 8	8. 3	0. 36	1. 95
比較例 2	1. 610	1. 592	11. 2	10. 5	0. 35	0. 63
比較例 3	1. 610	1. 591	11. 1	10. 3	0. 33	0. 70

[0019] If an example is compared with the example 1 of comparison, a difference remarkable to degradation of open circuit voltage will be accepted by 60 degrees C and 60-day storage, and a remarkable difference will be accepted also in the amount of hydrogen gas 60 degrees C and after 60-day storage. Therefore, by having formed in the inside of a can the electric conduction film which makes a graphite a principal component shows that the dissolution of the tin from a nickel-tin alloy layer was prevented, and the effect arose.

[0020] Moreover, if an example is compared with the examples 2 and 3 of comparison, improvement in the short-circuit current by the nickel-tin alloy layer can be checked. the difference with the example 1 of comparison which does not form the electric conduction film in a can inside clear-comes out

[0021]

[Effect of the Invention] As explained above, the alkaline cell of this invention became what was excellent in high capacity and the super-heavy-loading property, and was excellent also in the storage property by having added improvement to the container.

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 CLAIMS
 

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[Claim(s)]

[Claim 1] In the alkaline cell which inner-\*\*(ed) the power generation element in the metal can of the closed-end cylindrical shape which serves as a positive-electrode terminal As the above-mentioned metal can, a nickel-iron diffusion layer and a nickel-tin alloy layer are given to the side which becomes the can inside of a cold-rolled-steel-plate material base one by one. The alkaline cell characterized by using the thing in which the electric conduction film which makes a graphite a principal component was formed on the nickel-tin alloy layer by the side of a can inside after giving a nickel-iron diffusion layer to the side which becomes can superficies and carrying out drawing processing of this at the shape of a closed-end cylindrical can.

[Claim 2] a positive electrode -- a mixture -- the alkaline cell according to claim 1 whose inner rate of graphite addition is 8% or less

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APPL-NO: JP08236216

APPL-DATE: September 6, 1996

INT-CL (IPC): H01 M 2/02

## ABSTRACT:

PROBLEM TO BE SOLVED: To provide an alkaline battery whose properties are not deteriorated during a long time storage by improving a container of the alkaline battery.

SOLUTION: In an alkaline battery produced by filling a bottomed cylindrical metal can, which works also as a cathode terminal, with an electricity generating element, a metal can manufactured by the following steps is used as the metal can: forming a nickel-iron diffused layer 12 and a nickel-tin alloy layer 13 successively in the side, which becomes the inner face of a can, of a cold rolled steel sheet base, forming a nickel-iron diffused layer 10 in the side, which becomes the outer face of the can, press-drawing the resultant steel sheet into a bottomed cylindrical can, and then forming a conductive layer 14 mainly consisting of graphite on the nickel-tin alloy layer 13 in the can inner face side. Consequently, a battery whose properties are not deteriorated can be manufactured and especially, the battery is more efficient in the case the graphite addition ratio to the cathode active mix is controlled to be 8% or less for high capacity.

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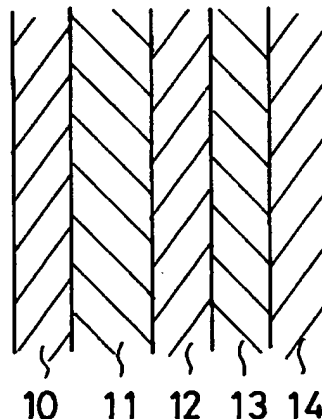
(54)【発明の名称】 アルカリ電池

(57)【要約】

【課題】アルカリ電池の容器に改良を加えて、長期の貯蔵で性能劣化を生じないアルカリ電池を提供する。

【解決手段】正極端子を兼ねる有底円筒形の金属缶内に発電要素を内填したアルカリ電池において、上記金属缶として、冷間圧延鋼板材素地の缶内面になる側にニッケル-鉄拡散層12およびニッケル-スズ合金層13を順次施し、缶外面になる側にニッケル-鉄拡散層10を施し、これを有底円筒型の缶状にプレス絞り加工した後、缶内面側のニッケル-スズ合金層13の上に黒鉛を主成分とする導電膜14を形成したものをを用いたことにより、性能劣化を生じない電池を形成する。特に、高容量化のために正極合剤中の黒鉛添加率を8%以下とした場合に、有用である。

金属缶外面



金属缶内面

## 【特許請求の範囲】

【請求項1】 正極端子を兼ねる有底円筒形の金属缶内に発電要素を内填したアルカリ電池において、上記金属缶として、冷間圧延鋼板材素地の缶内面になる側にニッケル-鉄拡散層およびニッケル-スズ合金層を順次施し、缶外面になる側にニッケル-鉄拡散層を施し、これを有底円筒型の缶状にプレス絞り加工した後、缶内面側のニッケル-スズ合金層の上に黒鉛を主成分とする導電膜を形成したものをを用いることを特徴とするアルカリ電池。

【請求項2】 正極合剤中の黒鉛添加率が8%以下である請求項1記載のアルカリ電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、アルカリ電池に関するものである。

## 【0002】

【従来の技術】ノート型パソコン、CDプレーヤ、MDプレーヤ、液晶テレビ等の携帯用AV機器、また、携帯電話などの超重負荷、重負荷の用途が最近のアルカリ電池に要求されてきている中で、従来、正極容器は鋼板の両面に予めニッケルメッキを施したものをプレス絞り加工するか、鋼板のみで絞り加工した後、ニッケルメッキを施してそれぞれ内面に黒鉛を主成分とする導電膜を形成している。

【0003】鋼板に予めニッケルメッキを施した場合は、容器にプレス絞り加工をするとニッケルメッキ表面にひび割れを生じて鉄の地肌が露出するので、ニッケルメッキの表面積が少なくなり、そのため全てニッケルメッキに覆われている条件に比べて接触抵抗が上昇する。また、鋼板のみで絞り、後でニッケルメッキを施した場合は外面側にはニッケルメッキが施されるが、内面側にはメッキのつき周りが悪い。例えば、外面側に3μmの厚さでニッケルメッキを施すと、内面側は0.5μm程度の厚さになる。このため正極合剤との接触が悪く、接触抵抗が高くなり短絡電流が低下して、長期の貯蔵では性能の劣化を招き水素ガスの発生量も増加する。これらの問題点を解決するために、正極容器内面には黒鉛を主成分とする導電膜が形成されている。

## 【0004】

【発明が解決しようとする課題】しかし、前述した超重負荷の用途では、これらの対策では不十分で、さらに改善する必要がある。特に、高容量化のために正極合剤中の黒鉛添加率を8%以下とした場合には、缶内面と正極合剤との接触抵抗が高くなるので、さらに改善する必要性が高い。

【0005】本発明は、上記問題に対処してなされたもので、アルカリ電池の容器に関して改良を加え、長期の貯蔵で性能劣化を生じないアルカリ電池を提供することを目的とするものである。

## 【0006】

【課題を解決するための手段】本発明では、アルカリ電池の容器に以下のような改良を加えて上記目的を達成した。すなわち、本発明は、正極端子を兼ねる有底円筒形の金属缶内に発電要素を内填したアルカリ電池において、上記金属缶として、冷間圧延鋼板材素地の缶内面になる側にニッケル-鉄拡散層およびニッケル-スズ合金層を順次施し、缶外面になる側にニッケル-鉄拡散層を施し、これを有底円筒型の缶状にプレス絞り加工した後、缶内面側のニッケル-スズ合金層の上に黒鉛を主成分とする導電膜を形成したものをを用いることを特徴とする。

【0007】上記したように、鋼板素地上にニッケル-鉄拡散層と更にその上にニッケル-スズ合金層を施したことによって、非常に硬い金属表面が得られる。プレス絞り加工時は表面のニッケル-スズ合金層が硬いために非常に細かいひび割れが発生し、細かい凸凹面を構成して正極合剤との接触向上に寄与する。また、ひび割れが発生したニッケル-スズ合金層の下には更にニッケル-鉄拡散層があるので、鋼板の地肌は露出しない。従って、接触抵抗が大きくなることはなく、短絡電流の向上が図れる。

【0008】また、ニッケル-スズ合金層が露出している場合には、合金層中のスズの溶解が起こることで、開路電圧の低下と水素ガスの発生があり、電池特性上問題となるが、本発明では、正極容器内面の電解液が接触する部分に、黒鉛を主成分とする導電膜が形成されているので、スズの溶解を防ぎ、開路電圧の低下を防止し、短絡電流が更に向上する。

【0009】また、発電要素を内填する端子兼容器である缶の外面がニッケル-鉄拡散層で覆われているため、通常のニッケルメッキに比べて接触抵抗が低く、また、ニッケル-鉄拡散層は非常に硬いため傷が付きにくいというメリットもある。

## 【0010】

【発明の実施の形態】以下、その実施例を図により詳細に説明する。図1は本発明の一実施例であるJIS規格LR6形(単3形)アルカリ電池の断面図である。また、図2は図1のアルカリ電池の金属缶1の断面構造を示す図である。

【0011】図1において、1は正極端子を兼ねる有底円筒形の金属缶、2は正極合剤、3はセパレータ、4はゲル状負極、5は負極集電棒、6は絶縁ガスケット、7はリング状金属板、8は金属封口板、9はラベルジャケットである。また、図2において、10はニッケル-鉄拡散層、11は鋼板、12はニッケル-鉄拡散層、13はニッケル-スズ合金層、14は黒鉛を主成分とする導電膜層である。

【0012】図1の電池の端子兼容器である金属缶1は次のように製造され、図2に示すような構成となる。す

なわち、冷間圧延鋼板材11をメッキ加工及び熱処理等により処理して、容器の内面側になる方にニッケル-鉄拡散層12、ニッケル-スズ合金層13が形成され、外面側にニッケル-鉄拡散層10が形成される。このように形成されたものを有底の円筒形にプレス絞り加工し、有底円筒形の缶状に加工後、内面に開口部のガスケットと接する箇所を除いた部分に黒鉛を主成分とする導電膜を形成する。導電膜の塗布方法は、黒鉛を主成分とする導電塗料をメチルエチルケトン(MEK)等の低沸点有機溶剤にて希釈し、スプレーガンより霧状に金属缶内面に塗布する。金属缶開口部のガスケットに接する部分は塗布されないようにする。導電塗料をスプレーガンにて塗布した後、乾燥機にて溶剤を蒸発させる。残った導電膜の厚さは1~10 $\mu$ m程度が望ましい。

【0013】この金属缶1内には円筒状に加圧成形した正極合剤2が充填されている。正極合剤2は、二酸化マンガン粉末と黒鉛粉末を混合し、これを金属缶1内に収納し所定の圧力で中空円筒状に加圧成形したものである。放電容量の高容量化のために正極合剤2中の黒鉛添加率(〔黒鉛粉末重量〕/[二酸化マンガン重量+黒鉛粉末重量])は8%とした。また、正極合剤2の中空部には、アセタール化ポリビニルアルコール繊維の不織布からなる有底円筒状のセパレータ3を介してゲル状負極4が充填されている。ゲル状負極4内には真鍮製の負極集電棒5が、その上端部をゲル状負極4より突出するように挿着されている。負極集電棒5の突出部外周面及び金属缶1の上部内周面には二重環状のポリアミド樹脂からなる絶縁ガスケット6が配設されている。また、ガスケット6の二重環状の間にはリング状の金属板7が配設され、かつ金属板7には負極端子を兼ねる帽子形の金\*30

\* 属封口板8が集電棒5の頭部に当接するように配設されている。そして、金属缶1の開口縁を内方に屈曲させることによりガスケット6及び金属封口板8で金属缶1内を密封口している。

【0014】(比較例1) 発電要素を内填する端子兼容器として、内面に黒鉛を主成分とする導電膜を形成していないこと以外は実施例と同様の缶を使用し、実施例と同様にしてJIS規格LR6形(単3形)アルカリ電池を組み立てた。

10 【0015】(比較例2) 発電要素を内填する端子兼容器として、予め冷間圧延鋼板材の内面側にニッケルメッキを施し、外面側にもニッケルメッキを施したものを、有底円筒形の缶状にプレス絞り加工し、さらに内面に黒鉛を主成分とする導電膜を形成した缶を使用した。それ以外は実施例と同様にしてJIS規格LR6形(単3形)アルカリ電池を組み立てた。

20 【0016】(比較例3) 発電要素を内填する端子兼容器として、冷間圧延鋼板材を有底円筒形の缶状にプレス絞り加工した後でニッケルメッキを施し、内面に黒鉛を主成分とする導電膜を形成した缶を使用した。それ以外は実施例と同様にしてJIS規格LR6形(単3形)アルカリ電池を組み立てた。

【0017】上記のようにして組み立てた各アルカリ電池について、60℃で10日及び60日貯蔵した後の、開路電圧(n=100個の平均値)、短絡電流(n=100個の平均値)、水素ガス量[水中で分解して電池内部のガスを捕集](n=100個の平均値)を調べた。表にこれらの結果を示す。

【0018】

【表1】

	開路電圧 (V)		短絡電流 (A)		水素ガス量 (CC)	
	10日後	60日後	10日後	60日後	10日後	60日後
実施例	1.610	1.594	14.0	12.5	0.34	0.56
比較例1	1.610	1.583	9.8	8.3	0.36	1.95
比較例2	1.610	1.592	11.2	10.5	0.35	0.63
比較例3	1.610	1.591	11.1	10.3	0.33	0.70

【0019】実施例と比較例1を比較すると、60℃、60日貯蔵で開路電圧の劣化に著しい差が認められ、また、60℃、60日貯蔵後の水素ガス量にも著しい差が認められる。したがって、缶の内面に黒鉛を主成分とする導電膜を形成したことにより、ニッケル-スズ合金層からのスズの溶解が防止されて、効果が生じたことが分かる。

【0020】また、実施例と比較例2及び3を比較すると、ニッケル-スズ合金層による短絡電流の向上が確認できる。缶内面に導電膜を形成していない比較例1との差は歴然である。

40※【0021】

【発明の効果】以上説明したように、本発明のアルカリ電池は、容器に改良を加えたことにより、高容量且つ超重負荷特性に優れ、また貯蔵特性にも優れたものとなった。

【図面の簡単な説明】

【図1】本発明の実施例であるJIS規格LR6形(単3形)アルカリ電池の断面図。

【図2】図1のアルカリ電池の金属缶1の断面構造を示す図。

※50 【符号の説明】

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1…金属缶、2…正極合剤、3…セパレータ、4…ゲル状負極、5…負極集電棒、6…絶縁ガスケット、7…リング状金属板、8…金属封口板、9…ラベルジャケット

ト、10…ニッケル-鉄拡散層、11…銅板、12…ニッケル-鉄拡散層、13…ニッケル-スズ合金層、14…黒鉛を主成分とする導電膜層。

【図1】



【図2】

